Hollandite in Hawaiian basalt: a relocation site for weathering-mobilized elements

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Abstract

Enrichments in Ba, REE and Y abundances, occurrences of REE, Y-bearing phosphate, depletions in K and Rb, and negative Ce anomalies in some lavas on Kahoolawe (Hawaii) reflect secondary mobilization of Ba, REE, Y, K and Rb. Hollandite (Ba-Mn-oxide) in the groundmass of a Kahoolawe lava contains nearly 10 wt.% BaO, ~ 1.1 wt.% CeO_2, and small amounts of La, Nd, Y, K, Na, P, Cl and Cu to provide an example of where elements mobilized during weathering processes on the Hawaiian Islands find residence. Fe-vernadite, a second Mn-oxide, also hosts mobilized REE and Ba. A positive Ce anomaly in the hollandite complements the negative Ce anomaly in some Kahoolawe lavas; this is analogous to Ce accumulation in todorokite of manganese nodules complementing Ce-depleted seawater. Mn-oxides, then, can serve as links between lavas depleted and enriched in certain elements.

KEYWORDS: hollandite, ferruginous vernadite, trace-element mobilization, Ce anomaly, Hawaiian basalt.

Introduction

THE whole-rock compositions of certain Hawaiian lavas indicate that minor elements were secondarily mobilized. One indication is anomalously low K and Rb abundances in some tholeiitic lavas of Kohala, Haleakala and Kahoolawe volcanoes (e.g. K_2O/P_2O_5 < 1.0; Feigensen et al., 1983; Chen and Frey, 1985; Fodor et al., 1992a). Other signs of secondary processes are occasionally observed as anomalously high Ba (e.g. > 600 ppm), rare-earth element (REE) (e.g. La > 200 ppm), and Y (e.g. > 100 ppm) abundances, and negative Ce anomalies (Roden et al., 1984; Clague, 1987; Lanphere and Frey, 1987; Fodor et al., 1992a).

Hawaiian lavas do not, as a rule, have petrographic features to suggest that profound trace-element mobilization occurred; generally

iddingsite associated with olivine is the only indication of some alteration. However, once whole-rock compositions for a sample set reveal that secondary processes did in fact mobilize various elements, a logical concern is to determine if and where these elements relocated in associated lavas. Thus far, the secondary mineral rhabdophane noted in a Kahoolawe Island, Hawaii, lava (Fodor et al., 1989; 1992b) demonstrates that some migrating REE and Y came to rest in a groundmass REE,Y-bearing phosphate. Here we expand the understanding of where mobile elements eventually take up residence by showing that secondary Mn-oxides can also serve as hosts for migrational elements such as Ba, K, REE and Y.

Background information

Shield volcano. Kahoolawe is a shield volcano forming an island 18 × 11 km (Fig. 1). Fodor et al (1992a) show that it is a tholeiitic shield at least 1.4

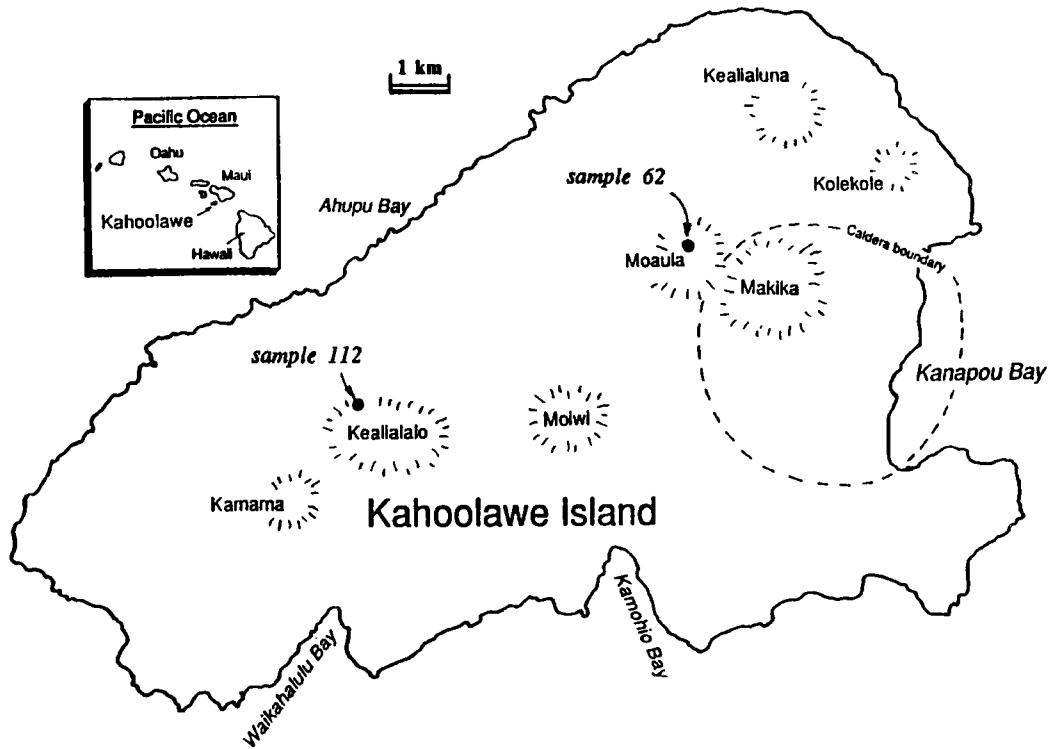[*]Present Address: Bass Enterprises Production, Ft. Worth, TX 76102, USA.

FIG. 1. Kahoolawe Island is one of the shield volcanoes making up the eight main Hawaiian Islands. Samples containing Mn-oxides for this study were collected from two vents on the shield, Kealialalo and Moaula (samples 112 and 62; Fodor *et al.*, 1992*a*).

Ma old, with intercalated tholeiitic and alkalic lavas as young as 1.15 Ma that erupted from late-stage shield and postshield vents. Field descriptions of Kahoolawe are limited to the early reports of Stearns (1940) and Macdonald (1940). One observation by those investigators that is pertinent to this report is that the island underwent significant alteration and soil formation, processes suitable for Mn-oxide formation (Nicholson, 1992).

Some of the postshield lavas are unusually enriched in *REE* and Y (Fig. 2), a feature rarely observed for Hawaiian lavas (other examples in Roden *et al.*, 1984; Clague, 1987). Electron-microbeam examinations of the groundmass of one *REE*,Y-enriched alkalic basalt sample revealed that the phosphate rhabdophane serving as a host for mobilized *REE* and Y contains ~ 6 wt.% La_2O_3 and ~ 8.5 wt% Y_2O_3 (Fodor *et al.*, 1989, 1992*b*) in grains 20–40 μm in size.

Basaltic lavas containing Mn-oxides. Sample 112 of Fodor *et al.* (1992*a*) has a composition transitional between tholeiitic and alkalic in terms of 3 wt.% Na_2O, 1.15 wt.% K_2O, 52.3

wt.% SiO_2, and *REE* enrichment relative to typical Hawaiian tholeiites (Fig. 2). It is also enriched in Ba, ~ 925 ppm. Through microscopy and electron microprobe analyses, we located a small (~ 100 μm), irregularly-shaped (Fig. 3) Ba-rich Mn-oxide grain along a boundary between a plagioclase crystal and the groundmass. Additional secondary phases in this lava are baryte (< 25 μm) in the groundmass and iddingsite that rims olivine.

Sample 62 of Fodor *et al.* (1992*a,b*) is alkalic basalt (K_2O 1.4 wt.%) with anomalously high *REE* and Y abundances (Fig. 2; La ~ 120–200 ppm; Y ~ 180 ppm), Ba enrichment (~ 650 ppm), and rhabdophane in the groundmass as a secondary host for *REE* and Y. Additionally, it has Ba-Mn oxides, baryte, and iddingsite rims on olivine. The Mn-oxide grain we selected to analyse is nearly 100 μm across and subangular (Fig. 4), and is within the groundmass but close to a cluster of plagioclase and olivine. It neighbours another Mn-oxide (Fig. 4) that was not analysed, but noted by microprobe that it has a thin (only a few μm) partial rim of rhabdophane.

Analytical procedures

We analysed the Mn-oxides (Table 1) with an ARL-EMX wavelength dispersive electron microprobe at NCSU. Reference minerals were spessartine for Mn, augite for Si, Ti, Al, Fe, Ca, Mg and Na, microcline for K, Ni-doped diopside for Ni, apatite, baryte and strontianite for P, Cl, Ba, S and Sr, pure Cu for CuO, and the Drake-Weill glass *REE* standards for La, Ce, Nd and Y. We applied Bence-Albee matrix corrections (using a beta factor of 1 for Cu).

Each analysis (Table 1) shows that the Ba-Mn oxides are about 8–9 wt.% short of a 100% sum. Other elements that we searched for but did not find in detectable amounts are Zn, Co, Rb, Nb and Zr, and we conclude that the low summations
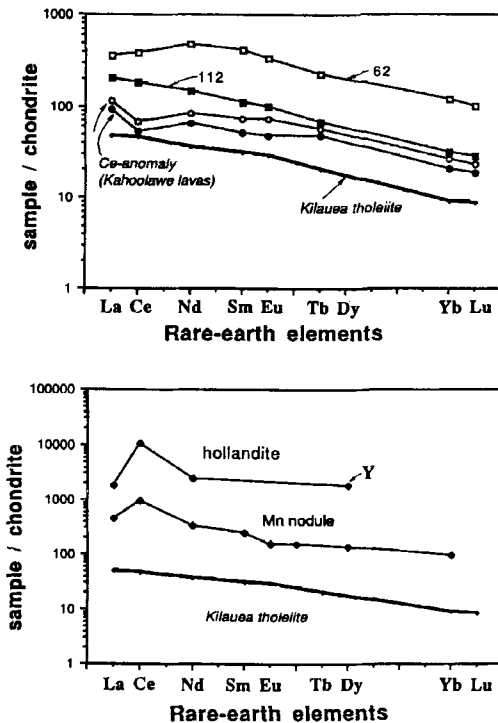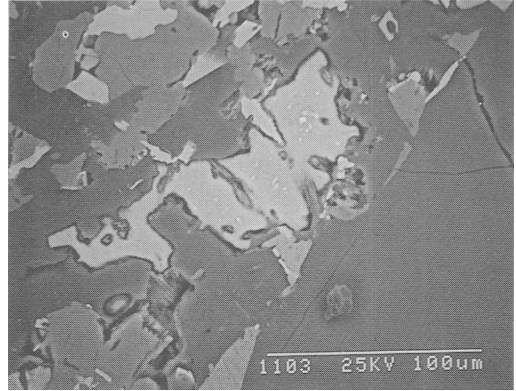

FIG. 3. A backscattered electron image of hollandite in the groundmass of sample 112 of Kahoolawe volcano (bright, central area). The analysis in Table 1 is an average of ~25 spots across all of the four areas comprising the irregularly-shaped grain.

are due to water content. The measured Mn contents (Table 1) are recalculated to express Mn as Mn^{3+} and Mn^{4+} because Mn occurs in these oxidation states in the kinds of Mn-oxides examined here (e.g. Post *et al.*, 1982). Best fits for structural formulae used a $Mn^{3+}:Mn^{4+}$ ratio of 15:85. All Fe and Ce are expressed in their highest oxidation states.

Barium is a substantial component in the Mn oxides and we therefore needed to account for the overlap of the Ba-$L\beta_1$ peak with the Ce-$L\alpha_1$ peak. Our procedure was to determine the intensity (as counts/second) for Ba at both its analysis peak

FIG. 2. (top) Rare-earth element (*REE*) patterns for four Kahoolawe lavas showing *REE* enrichments in samples 62 and 112, negative Ce-anomalies in the other two (samples 114 and 127; all samples from Fodor *et al.*, 1992*a*), and a comparative reference to the *REE* pattern for historic Kilauea tholeiite (Budahn and Schmitt, 1985). (bottom) *REE* patterns for hollandite in sample 112 (note: element Y replaces Dy position in pattern) and for a Mn-nodule (sample wah 2 pg of Elderfield *et al.*, 1981), both with positive Ce anomalies, compared to historic Kilauea tholeiite.
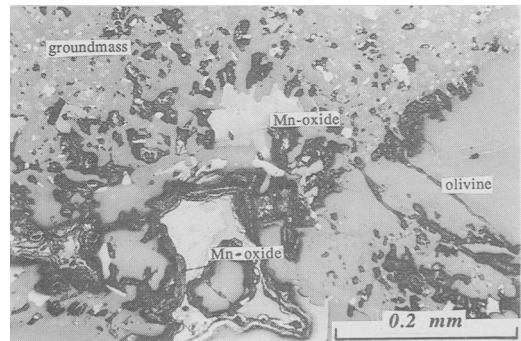

FIG. 4. A reflected-light photomicrograph of Mn-oxides (two bright, labelled areas near centre) in Kahoolawe lava sample 62. Table 1 lists the analysis for the lower grain, a ferruginous vernadite; the composition is the average of ~25 spot analyses from the central area of the grain.

TABLE 1. Compositions (in wt. %) for *REE*, Y-bearing hollandite and ferruginous vernadite in lavas of Kahoolawe Island, Hawaii

	Hollandite	formula $O = 16$	Fe-vernadite	formula $O = 12$
SiO_2	12.3	1.620	11.8	1.193
TiO_2	0.28	0.028	0.23	0.017
Al_2O_3	2.9	0.450	2.2	0.262
$Fe_2O_3^*$	3.3	0.326	29.1	2.209
$Mn_2O_3^*$	8.0	0.802	4.9	0.377
MnO_2^*	49.7	4.523	30.9	2.159
MgO	0.18	0.035	0.82	0.124
CaO	0.63	0.089	0.58	0.063
Na_2O	0.44	0.112	0.48	0.094
K_2O	0.57	0.096	0.25	0.032
P_2O_5	0.88	0.098	2.1	0.180
Cl	0.85	0.190	0.08	0.014
CuO	0.28	0.028	0.08	0.006
BaO	9.7	0.501	6.1	0.242
NiO	0.06	0.006	n.d.	
SrO	0.04	0.003	n.d.	
SO_3	0.06	0.006	n.d.	
La_2O_3	0.07	0.003	< 0.01	
CeO_2	1.1	0.051	0.20	0.007
Nd_2O_3	0.18	0.008	0.12	0.004
Y_2O_3	0.45	0.032	0.20	0.011
Subtotal	91.97	9.007	90.14	6.994
$-O = Cl$	0.19		0.02	
Sum	91.78		90.12	
$H_2O^\dagger$	8.0	3.517	9.0	3.037
Total	99.78		99.12	

* MnO was analysed as 47.7 wt.% (sample 112) and 29.7 wt.% (sample 62) but recalculated to a ratio of 15:85 $Mn^{3+}:Mn^{4+}$; all Fe as Fe_2O_3 and all Ce as CeO_2.
† H_2O estimated by difference from 100%.
Analyses are average compositions of ~ 25 points on a grain

($L\alpha_1$) and the Ce analysis peak ($L\alpha_1$). Two minerals, benitoite and baryte (both Ce-free), produced 52.3% and 53.1% of their Ba-$L\beta_1$ intensity respectively (after subtracting background intensities) as Ba interference on the Ce-$L\alpha_1$ peak (for analysis of Ce). To quantitatively analyse for Ce in our Mn-oxides, we then determined 52.7% of the Ba-$L\alpha_1$ intensity at a particular spot on the Mn oxide and subtracted that value from the Ce-$L\alpha_1$ intensity of the Ce peak at that same spot on the Mn oxide.

Results

The composition of the Mn-oxide in lava sample 112 (Table 1) is an average of ~ 25 spot analyses at various positions across the grain, and it has BaO contents of 9.7 wt.%. Of the two common Ba-bearing Mn oxides, romanechite and hollandite (Turner and Buseck, 1979), our formula calculation (Table 1) best fits that for hollandite, which is based on 16 oxygens (general: $A_{1-2}B_8O_{16}$, where A = large ions, such as Ba and K; Post and Burnham, 1986). The water content of 8 wt.%, estimated by difference, from 100%, is high compared with other determinations, which show $H_2O < 2$ wt.% (Bystrom and Bystrom, 1950; Bish and Post, 1989). We therefore attribute a large portion of the estimated water content to adsorbed, in addition to structural water.

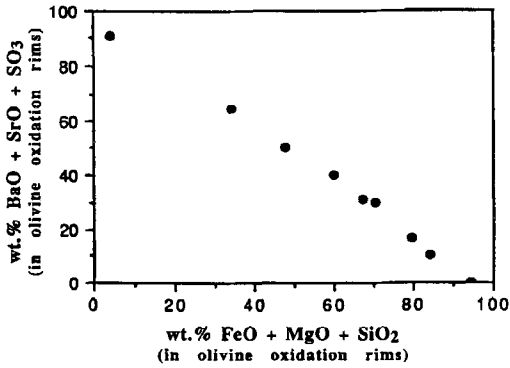The tunnel structure of hollandite (Turner and Buseck, 1979) can accommodate large mono- and

FIG. 5. Abundances of the minor, mobile elements Ba, Sr and S co-vary with those of the major components Fe, Mg and Si in oxidation rims on olivine in alkalic basalt sample 62 of Fodor *et al.* (1992*a*). Each point represents an average composition for 3–5 spot analyses by microprobe on a local region. Compositions on these oxidation rims range from iddingsite (essentially hydrated Fe–Mg silicate) to baryte; Table 2 lists representative compositions.

divalent cations (e.g. > 0.9 Å radius), and typically H_2O molecules and K, Sr, and Na are present in addition to Ba (e.g. Post *et al.*, 1982). Rare earth elements and Y are therefore appropriate for this Ba-Mn oxide, as they are for the tunnel structure of the Mn oxide todorokite (Elderfield *et al.*, 1981). A *REE* pattern (Fig. 2) shows abundances

> 1000 times chondritic values and a positive Ce anomaly. In addition to significant Ba, *REE*, Y, Na, K and Ca contents (Table 1), the hollandite includes the large Cl ion in amounts substantial enough to manifest a peak in an energy dispersive scan (Fig. 6). The microprobe analyses showed, however, that Cl has irregular distribution across the hollandite. That is, the compositional range determined for 25 analysis points is 0.4–1.8 wt.% and the mean is 0.85 wt.% Cl. Because of the tunnel structure of hollandite, we believe it is more reasonable to include Cl with the other large ions in the structural formula rather than to substitute Cl for oxygen anions in the formula (Table 1).

Other pertinent features include the relatively high SiO_2 content. Only a small portion, if any, of the 12.3 wt.% could be attributed to grain boundary excitation, and the high SiO_2 content is intrinsic to the Mn-oxide and appropriate for its origin in a silicate matrix. The P_2O_5 detected by wavelength dispersion is not apparent in the energy scan (Fig. 6), probably due to the intense neighbouring Si peak.

The composition for Mn-oxide in the Kahoolawe lava sample 62 (Fodor *et al.*, 1992*a*) is the average of ~25 spots in the central area of the grain (Fig. 4). This Mn-oxide has lower BaO (6.1 wt.%) and *REE* and Y contents (< 0.2 wt.% Ce and Y), but similar SiO_2 (11.8 wt.%) when compared to the hollandite in sample 112 (Table 1). Also, it has much less Cl but a large amount of P_2O_5 that ranges 1.5–4.0 wt.% on point-by-point
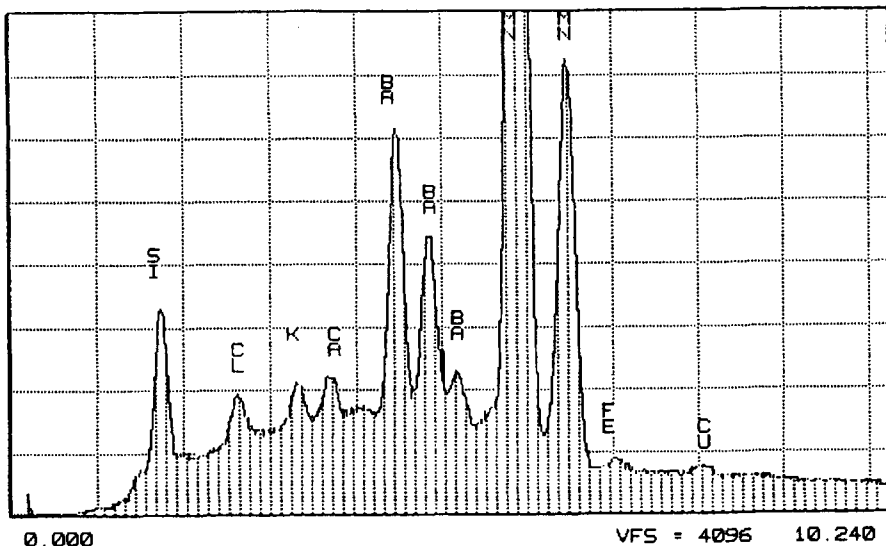

FIG. 6. An energy-dispersive scan of a point on hollandite (Fig. 3) in sample 112 with labelled peaks. A Ce peak is not resolved among the strong Ba peaks.

TABLE 2. Average compositions (in wt.%) for representative Ba-, Sr and S-bearing portions of oxidation (iddingsite) rims on olivine phenocrysts in Kahoolawe lava sample 62.

	1	2	3	4
SiO_2	32.4	26.5	15.1	2.0
TiO_2	0.11	0.18	0.24	0.38
Al_2O_3	0.63	0.71	0.77	0.66
FeO	30.1	26.3	13.2	1.1
MnO	0.27	0.24	0.19	0.18
MgO	21.6	14.3	5.8	0.87
CaO	0.35	0.50	0.76	0.55
Na_2O	0.02	0.13	0.21	0.40
K_2O	0.04	0.11	0.15	0.17
P_2O_5	0.52	0.68	0.36	0.19
SO_3	4.0	11.3	21.7	30.9
SrO	0.81	1.7	5.1	2.2
BaO	5.3	17.8	37.5	58.0
Total	96.15	100.45	101.08	97.78

each column is the average of 3−5 analysis spots: col. 4 is baryte.

microprobe analyses (mean of 2.1 wt.%).

Based on the relatively high Fe/Mn ratio, it is ferruginous vernadite, a Mn-oxide commonly observed in a marine environment (Ostwald, 1984; Bolten et al., 1988). The structure of vernadite is not fully understood and, according to Manceau et al. (1992), vernadite is probably a hybrid between phyllo- and tectomanganate. Our structural formula in Table 1 is a good match for seven cations for 12 oxygen anions, the ratio for todorokite, a Ba-bearing tectomanganate (Burns et al., 1983).

Barium is also present in sample 62, along with Sr and S, in portions of oxidation rims (iddingsite?) on some olivine phenocrysts. Figure 5 shows that Ba, S and Sr abundances in some oxidation rims co-vary with the main components of typical iddingsite, Fe, Mg, and Si. Table 2 presents four representative compositions.

Discussion

Hollandite and Fe-vernadite in Kahoolawe Island basaltic rocks manifest secondary mineralization associated with the weathering of this shield volcano. That is, these secondary minerals owe their origins to the relatively high solubility of Mn from source rocks and subsequent transportation in surface and groundwaters (Frakes and Bolten, 1992); eventual high Eh-pH conditions caused precipitation of Mn oxide (e.g. Hem, 1972;

Ostwald, 1992). Of relevance is the fact that the Mn oxide phases served as hosts for elements that became mobilized during weathering, alteration and soil formation processes. As a pair composed of different Mn-oxides, the hollandite and ferruginous vernadite show that certain minor element abundances correlate with Fe and Mn abundances, which is consistent with observations made for Fe−Mn sediment coatings (Buckley, 1989), Fe-Mn concretions (Rankin and Childs, 1976), and for Mn nodules (Elderfield et al., 1981). Namely, higher P_2O_5 attends increasing Fe, while Ce, total REE, and the metals Cu and Ni correlate with Mn (Table 1).

Of special interest to the geochemistry of Hawaiian lavas is that the hollandite and Fe-vernadite scavenged K and Ce, both of which were noted (Fodor et al., 1992a) to have comparatively low (e.g. < 0.20 wt.% K_2O) abundances in some Kahoolawe lavas, presumably due to leaching. These phases therefore identify some destinations for the K and Ce noted to be 'missing' from some whole-rock compositions of Hawaiian lavas (Feigensen et al., 1983; Chen and Frey, 1985; Lanphere and Frey, 1987). The hollandite and ferruginous vernadite also attest to P, Cl, metals and other alkalis (Ba and Na) having been mobilized by secondary processes that might otherwise go undetected by conventional whole-rock analyses. Similarly, the Ba, Sr and S abundances in oxidation rims on olivine also reflect mobilization of minor elements.

In addition to Ce, the Mn oxides appear to have accommodated appreciable amounts of total REE and Y that were transient due to a seemingly rare secondary process that leaches these elements from Hawaiian lavas (Fodor et al., 1992a). While this is not the first indication that Mn-oxides in terrestrial environments can fix mobile REE and Y (e.g. Rankin and Childs, 1976; REE in Fe-Mn concretions), it appears to be the only report that such high REE concentrations (e.g. La > 500 ppm) can occupy specific terrestrial Mn-oxides.

While details of REE and Y mobilization and Eh-pH for secondary mineralization are not objectives here, the reasons for the normally weathering-resistant REE and Y, and for high Ce relative to other REE, coexisting with Ba, K, Na, Cu, P and Cl in Mn oxides in Hawaiian lavas are nonetheless pertinent. Studies of REE behaviour during weathering of geologic material show that REE can be liberated from apatite under acidic conditions, and the subsequent stability of light-REE and heavy-REE complexes in groundwater depends on pH, alkalinity, and carbonate content (Lottermoser, 1990). Changes in these conditions can fractionate groups of light-REE from heavy-

REE. Once in solution, Ce behaviour may deviate from that of the other *REE* because it oxidizes from trivalent to tetravalent states and becomes less mobile. The extensive weathering process of Kahoolawe (Stearns, 1940) probably provided the Eh needed to preferentially precipitate Ce^{4+} in the Mn oxides over other *REE*.

In the marine environment, oxidized Ce finds its way into the todorokite of manganese nodules (Elderfield *et al.*, 1981). However, as noted in a report on Ce behaviour in laterite profiles by Braun *et al.* (1990), the geochemistry of Ce in continental environments is not well documented. The roles of hollandite and ferruginous vernadite as 'sinks' for Ce relative to total *REE* in Kahoolawe lavas therefore improve the profile of understanding of Ce geochemistry on land because the Ce source (the lavas) and original concentrations are known (e.g. Ce ~22–40 ppm in tholeiites; Budahn and Schmitt, 1985). This 'sink' characteristic is analogous to Ce behaviour in the marine environment where, as Fig. 2 shows, todorokite in Mn nodules acquires a positive Ce anomaly. The occurrence of high Ce abundances relative to total *REE* in hollandite and the negative Ce anomalies in some Kahoolawe lavas (Fig. 2), then, parallel the todorokite-seawater complementary relationship of respective positive-negative Ce anomalies (Fleet, 1984).

From a basalt geochemistry point of view, the main importance of trace element-bearing hollandite and Fe-vernadite is in their roles as liaison between the Kahoolawe lavas that contain clear evidence for leaching of K, Rb and Ce, and those lavas enriched in Ba, *REE* and Y (Fig. 2 and Fodor *et al.*, 1992 a,b). Closer examination of lavas on other Hawaiian islands and elsewhere with low K_2O/P_2O_5 ratios (e.g. Mauna Kea; Frey *et al.*, 1990), *REE*, Y and Ba enrichment (e.g. Tertiary basalts, Australia; Price *et al.*, 1991), and negative Ce anomalies may reveal that they, too, have Mn oxides in associated lavas that serve as hosts for leached and mobilized labile elements and oxidized Ce.

Acknowledgements

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